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BOX PCT

Assistant Commissioner for Patents
 Washington, D.C. 20231

PCT/JP00/07443
 -filed October 24, 2000

Re: Application of Hiroshi UCHIDA, Tomoyoshi HIGASHI, Etsuko KADOWAKI, Takashige MIYANARI and Wataru OGUCHI
 PROCESS FOR PRODUCING ESTERS
 Our Ref: Q58538

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter I of the Patent Cooperation Treaty:

- ☒ an executed Declaration and Power of Attorney.
- ☒ an English translation of the International Application.
- ☒ three (3) sheet(s) of informal drawings.
- ☒ an executed Assignment and PTO 1595 form.

The Form PTO-1449 listing the International Search Report (ISR) references and a complete copy of each reference will be submitted at a later date.

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

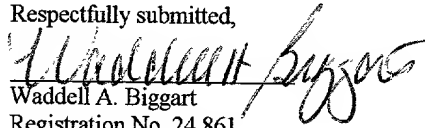
The Government filing fee is calculated as follows:

Total claims	24	-	20	=	4	x	\$18.00	=	\$72.00
Independent claims	3	-	3	=		x	\$80.00	=	\$0.00
Base Fee									\$860.00
Multiple Dependent Claim Fee									\$270.00
TOTAL FILING FEE									\$1202.00
Recordation of Assignment									\$ 40.00
TOTAL FEE									\$1242.00

Checks for the statutory filing fee of \$1202.00 and Assignment recordation fee of \$40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from October 25, 1999, February 25, 2000, and March 29, 2000, based on JP Application Nos. 11-301780 (Pat. Appln.), 2000-49627 (Pat. Appln.), and U.S. Provisional Application No. 60/192,880 (Pat. Appln.), respectively.

Respectfully submitted,


 Waddell A. Biggart
 Registration No. 24,861

WAB/plr

3/PAT

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DESCRIPTION

PROCESS FOR PRODUCING ESTERS

Cross-Reference to related Applications

5 This application is an application filed under
35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C.
§119(e)(1) of the filing date of the Provisional
Application 60/192,880 filed March 29, 2000, pursuant to
35 U.S.C. §111(b).

10 Technical Field

The present invention relates to a process for
producing an ester by reacting an ethylene and a
carboxylic acid.

Background Art

15 It is well known that a lower olefin and a lower
aliphatic carboxylic acid react in the presence of an
acid catalyst to provide the corresponding ester. It is
also known that in this reaction, a heteropolyacid and/or
heteopolyacid salt effectively act as a catalyst.

20 Specific examples of these conventional techniques
include those described, for example, in Japanese
Unexamined Patent Publications No. 4-139148, No. 4-
139149, No. 5-65248, No. 5-163200, No. 5-170699, No. 5-
255185, No. 5-294894, No. 6-72951 and No. 9-118647.

25 Thus, the development of catalysts having high initial
activities is proceeding.

However, in industrial production processes,
impurities derived from the starting materials or by-
products produced during the reaction cause deterioration
30 of the catalyst and in turn the reaction yield
disadvantageously decreases. Particularly, in the
process having a circulation system, if a reaction is
continuously performed for a long time, various
impurities or by-products accumulate in the system and
35 due to the effect thereof, for example, a vicious circle
arises such that the catalyst deteriorates and the side
reaction is further accelerated.

Disclosure of Invention

It is an object of the present invention to provide a process for producing an ester by esterifying a carboxylic acid with ethylene in a vapor phase, where the operation can be continuously and stably performed for a long period of time.

In particular, the object of the present invention is to provide the above-described process for producing an ester where, in a process having a circulation system, the impurities derived from the starting materials or the compounds derived from the by-products produced by a side reaction are reduced to a low concentration with respect to the starting materials, so that the catalyst can be prevented from deteriorating and, in turn, the operation can be continuously and stably performed for a long period of time.

The present inventors have made extensive studies to investigate a process for producing an ester, by reacting ethylene and a carboxylic acid, in which deterioration of the catalyst hardly occurs and the operation can be continuously and stably performed over a long period of time.

As a result, it has been found that, in a process for producing an ester by esterifying a carboxylic acid and an ethylene using an acid catalyst in a vapor phase, when the concentration of olefin having 3 or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene, the deterioration of the catalyst can be remarkably prevented from proceeding and in turn, a continuous and stable operation can be performed for a long time.

It has also been found that, in the process for producing an ester by esterifying a carboxylic acid and ethylene using an acid catalyst in a vapor phase, when the concentration of olefin equivalent in the starting materials is controlled to 50,000 ppm or less in terms of

the molar ratio to the total of the olefin equivalent and ethylene, the deterioration of the catalyst can be remarkably prevented from proceeding and a continuous and stable operation can be performed for a long time, as in the above-mentioned process.

Brief Description of Drawings

Fig. 1 is a schematic view showing a one-path process according to the invention having no circulation step, wherein acetic acid is used as a carboxylic acid.

Fig. 2 is a schematic view showing a process according to the invention having a circulation step from subsequent step, wherein acetic acid is used as a carboxylic acid.

Fig. 3 is a schematic view of a testing apparatus used in the examples.

Best Mode for Carrying Out the Invention

The present invention is described in detail below.

The term "olefin having 3 or more carbon atoms" as used herein generally refers to one or more olefins except for ethylene. Specific examples thereof include linear terminal olefins having 3 or more carbon atoms, such as propylene, 1-butene, 2-butene, isobutene, 1-hexene and 2-octene, internal olefins, branched terminal olefins, branched internal olefins, and cyclic olefins having 3 or more carbon atoms, such as cyclopentene and cyclohexene.

Among these, so-called ethylene oligomers derived from an ethylene and produced by the side reaction which may occur under the esterification reaction conditions, such as 1-butene, cis-2-butene, trans-2-butene, 2-methyl-2-pentene and 3-methyl-2-pentene, have a possibility of causing a problem. Of course, the olefins are not limited thereto.

The term "olefin equivalent" as used herein refers to one or more compounds which can produce the olefin having 3 or more carbon atoms under the esterification reaction conditions. Specific examples thereof include

hydrates of olefins having 3 or more carbon atoms, ether compounds produced by the reaction of the hydrate with ethylene or an olefin having 3 or more carbon atoms, and carboxylic acid esters produced by the reaction of a carboxylic acid with an olefin having 3 or more carbon atoms. However, the olefin equivalent is not limited thereto and all compounds are included as long as they are compounds capable of producing an olefin having 3 or more carbon atoms under the esterification reaction conditions.

Specific examples of the olefin equivalent include the following compounds.

Examples of the hydrate of an olefin having 3 or more carbon atoms include isopropanol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol and 2-hexanol.

Examples of the ether compound produced by the reaction of a hydrate of an olefin having 3 or more carbon atoms with ethylene or an olefin having 3 or more carbon atoms include ethyl isopropyl ether, ethyl sec-butyl ether, ethyl t-butyl ether, di-sec-butyl ether, di-n-butyl ether and ethyl cyclohexyl ether.

Examples of the carboxylic acid ester produced by the reaction of a carboxylic acid with an olefin having 3 or more carbon atoms include isopropyl acetate, sec-butyl acetate, sec-butyl propionate, t-butyl acetate and cyclohexyl acetate.

These compounds, namely, hydrates of olefins, ether compounds and carboxylic acid esters, are the specific examples of the equivalent of an olefin. However, needless to say, the specific examples of the olefin equivalent is not limited thereto.

The olefin equivalent also includes those produced in the reaction system as well as those contained in the starting materials newly fed to the reaction system.

Particularly, in performing the process for producing an ester by the esterification reaction of a carboxylic acid and ethylene using an acid catalyst in a

vapor phase, when water is present in the system, there is a possibility that a hydrate may be produced by the hydration of ethylene and also an ether compound or a carboxylic acid ester is further produced from the hydrate. Furthermore, when a circulation system for the unreacted raw materials is integrated into the production process of an ester so as to improve the yield or the like, the hydrate, the ether compound and the carboxylic acid ester produced in the reaction system may disadvantageously mingle with the unreacted starting materials. In this document, the "olefin equivalent" as used herein includes the hydrates, ether compounds and carboxylic acid esters produced in the reaction system by the esterification reaction.

In the process for producing an ester according to the present invention, the concentration of olefin having 3 or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene, which is effective in reducing the deterioration rate of the catalyst and in turn continuously and stably performing the operation for a long period of time.

The terms "the concentration of olefin having 3 or more carbon atoms in the starting materials" and "the concentration of olefin equivalent in the starting materials" each refers to a concentration immediately before the inlet of a reactor for performing the esterification reaction.

For example, specifically, in the case where the reaction is performed in the one-path process having no circulation step as shown in Fig. 1, the concentration immediately before the inlet of a reactor indicated by (1) applies. In the process having a circulation step from a subsequent step as shown in Fig. 2, the concentration immediately before the inlet of a reactor indicated by (2) applies. Needless to say, the present invention is by no means limited to these exemplified

processes.

Accordingly, the term "starting materials" as used herein of course includes those obtained by recovering unreacted starting materials, through a subsequent step such as separation of the objective compound, after the reaction and supplied to the reactor via a circulation system, in addition to ethylene and acetic acid newly fed to the reaction system.

The position (1) in the process shown in Fig. 1 and the position (2) in the process shown in Fig. 2 are both kept at a temperature equal to or higher than the reaction temperature in the reactor. Accordingly, to measure the concentration at such a position, the sampling must be particularly designed.

In particular, some olefin equivalents are readily condensed when cooled to room temperature and, therefore, to avoid measurement errors due to the effect thereof, the sampling must be designed, for example, to separate the condensed components from the non-condensed components by cooling them using an ice trap or the like and analyze respective components.

If the concentration of olefin having 3 or more carbon atoms in the starting materials exceeds 10,000 ppm in terms of the molar ratio to the total of the olefin and ethylene, the catalytic activity decreases at an extremely high rate and, as a result, the catalyst life is greatly shortened. This is thought to occur because the above-described olefin reacts with ethylene on the catalyst to produce cokes and the active sites of the catalyst are covered by the cokes to cause the deactivation.

Accordingly, the concentration of olefin having 3 or more carbon atoms in the starting materials is preferably as low as possible. These olefins cannot be completely removed with ease, but the concentration is preferably 5,000 ppm or less, more preferably 1,000 ppm or less.

The method for controlling the concentration of

olefin having 3 or more carbon atoms in the starting materials to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene is not particularly limited. Commonly known separation techniques may be used.

As an example, fundamentally, ethylene used as a starting material should of course be refined to reduce the contents of these compounds as much as possible.

The olefin having 3 or more carbon atoms produced by the side reaction within the reaction system, which becomes a problem when a circulation system is integrated, can be separated from the ethylene by a method of allowing an appropriate solvent to absorb the main products exclusive of the ethylene, the starting materials and the by-products in the reaction gas discharged from the reactor. Also, the raw material gas may be separated from ethylene by high-pressure or low-temperature distillation or by using a separation membrane or the like. Other than these specific examples, any method may be used as long as it is a method capable of controlling the concentration of the olefin having 3 or more carbon atoms circulated and guided to the reactor to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene.

If the concentration of olefin equivalent in the starting materials exceeds 50,000 ppm in terms of the molar ratio to the total of the olefin equivalent and ethylene, similarly to the case where the concentration of olefin having 3 or more carbon atoms exceeds 10,000 ppm in terms of the molar ratio to the total of the olefin and ethylene, the catalytic activity decreases at an extremely high rate and, as a result, the catalyst life is greatly shortened.

Although it may slightly differ depending on the individual olefin equivalents, the olefin equivalent generally exhibits an activity of deteriorating the catalyst on the same level as the olefin having 3 or more

carbon atoms when the concentration thereof is about 5 times higher. This difference is considered to result from the fact that the olefin equivalent produces an olefin after being decomposed on the catalyst and, therefore, the effect on the deactivation is low even if the concentration is higher than that of the olefin.

However, similarly to the olefin having 3 or more carbon atoms, the concentration of the olefin equivalent is preferably as low as possible. Although complete removal of the olefin equivalent may not be attained with ease, the concentration thereof is preferably 25,000 ppm or less, more preferably 5000 ppm or less.

The method for controlling the concentration of olefin equivalent in the starting materials to 50,000 ppm or less in terms of a molar ratio to the total of the olefin equivalent and ethylene is not particularly limited. Similarly to the olefin having 3 or more carbon atoms, commonly known separation techniques may be used for the olefin equivalent.

When the olefin having 3 or more carbon atoms and the olefin equivalent are present together, an interaction therebetween is not particularly observed. Roughly, the sum of one-fifth the concentration of all olefin equivalents and the concentration of olefin having 3 or more carbon atoms in the starting materials is preferably 10,000 ppm or less in terms of the molar ratio to the total of the olefin and olefin equivalent and ethylene.

Needless to say, similarly to their individual concentrations, the concentration here is also preferably as low as possible and, specifically, it is preferably 5,000 ppm or less, more preferably 1,000 ppm or less.

The method for measuring the concentration of the olefin having 3 or more carbon atoms or the olefin equivalent is not particularly limited and any method may be used as long as it is a method commonly used for measuring the concentration. Specific examples of the

measuring method include a method of placing a cell in a part of the apparatus and spectro-optically measuring the concentration using an appropriate wavelength, and a method of sampling a part of the starting material and analyzing it by gas chromatography. However, the present invention is by no means limited thereto.

The optimal measuring method varies depending on the properties of the object to be measured or the environment of the measurement, but a method which is free of any effect from other components is favored with good quantitation and reproduction, is low in measuring threshold value, and is simple and inexpensive, is preferred.

The carboxylic acid for use as a reaction starting material in the present invention is a lower aliphatic carboxylic acid having from 1 to 4 carbon atoms. Preferred are formic acid, acetic acid, acrylic acid, propionic acid and methacrylic acid, and more preferred are acetic acid and acrylic acid.

The acid catalyst for use in the present invention is a compound widely used as an acid catalyst such as ion-exchange resin, mineral acid, heteropolyacid, zeolite and composite metal oxide. Preferred are a heteropolyacid and a heteropolyacid salt. A heteropolyacid is a compound consisting of a center element and peripheral elements to which oxygen is bonded.

The center element is usually silicon or phosphorus but not limited thereto and the center element may be any one selected from the elements belonging to Groups 1 to 17 of the Periodic Table. The Periodic Table as used herein indicates the Periodic Table provided in Muki Kagaku Meimeiho, Kaitei-Ban (Nomenclature in Inorganic Chemistry, Revised), Kokusai Junsei Oyobi Oyo Kagaku Rengo (1989).

Specific examples of the center element include cupric ion; divalent beryllium, zinc, cobalt and nickel ions; trivalent boron, aluminum, gallium, iron, cerium,

arsenic, antimony, phosphorus, bismuth, chromium and rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulfur, tellurium, manganese, nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium and antimony ions; hexavalent tellurium ion; and heptavalent iodide ion, but the present invention is by no means limited thereto.

Specific examples of the peripheral element include tungsten, molybdenum, vanadium, niobium and tantalum, but the present invention is not limited thereto.

These heteropolyacids are also known, e.g., as "polyoxoanion", "polyoxometallate" or "metal oxide cluster". The structures of some of the well known anions are known, for example, as Keggin, Wells-Dawson or Anderson-Evans-Perloff structures. Heteropolyacids usually have a high molecular weight, for example, a molecular weight, e.g., in the range of 700 to 8,500 and include dimeric complexes.

The heteropolyacid salt is not particularly limited as long as it is a metal salt or onium salt resulting from substituting a part or all of the hydrogen atoms of the heteropolyacid.

Specific examples thereof include metal salts, e.g., such as of lithium, sodium, potassium, cesium, magnesium, barium, copper, gold and gallium, and onium salts such as of ammonia, but the present invention is not limited thereto.

Particularly when the heteropolyacid is in a free acid form or in a certain salt form, the heteropolyacid has a relatively high solubility in polar solvents such as water or other oxygenated solvents, and the solubility can be controlled by selecting the appropriate counter ions.

Examples of the heteropolyacid which can be particularly preferably used as a catalyst in the present invention include:

Tungstosilicic acid	$H_4[SiW_{12}O_{40}] \cdot xH_2O$
Tungstophosphoric acid	$H_3[PW_{12}O_{40}] \cdot xH_2O$
Molybdophosphoric acid	$H_3[PMo_{12}O_{40}] \cdot xH_2O$
Molybdosilicic acid	$H_4[SiMo_{12}O_{40}] \cdot xH_2O$
Vanadotungstosilicic acid	$H_{4+n}[SiV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdophosphoric acid	$H_{3+n}[PV_nMo_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstosilicic acid	$H_{4+n}[SiMo_nW_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$

wherein n is an integer of 1 to 11 and x is an integer of at least 1.

Particularly preferred examples of the heteropolyacid salt include lithium salts, sodium salts, potassium salts, cesium salts, magnesium salts, barium salts, copper salts, gold salts, gallium salts and ammonium salts of the above-described heteropolyacids which are particularly preferred.

The acid catalyst may be supported on a support. In this case, the acid catalyst content is preferably from 10 to 200 mass%, more preferably from 50 to 150 mass%, based on the entire mass of the support.

If the acid catalyst content is less than 10 mass%, the content of active components in the catalyst may excessively be lower and the activity per the catalyst unit mass may disadvantageously decrease.

If the content of the acid catalyst exceeds 200 mass%, the effective surface area may decrease and, as a result, the effect owing to the increase in the supported

amount may not be brought out and at the same time, coking is disadvantageously liable to occur to greatly shorten the catalyst life.

The substance which can be used as a support for the acid catalyst of the present invention is not particularly limited and those capable of providing, when prepared as a catalyst by carrying the acid catalyst, a catalyst having a specific surface area of from 65 to 350 m²/g, as measured by BET method, is preferred.

The shape of the substance which can be used as a support for the catalyst of the present invention is not particularly limited and, specifically, a powder, spheres, pellets and any other forms may be used. Specific examples thereof include silica, diatomaceous earth, montmorillonite, titania, activated carbon, alumina and silica-alumina, but the present invention is not limited thereto.

The support is preferably a support comprising a siliceous main component and having a spherical or pellet shape, more preferably a silica having a purity of 95 mass% or more based on the entire mass of the support.

The average diameter thereof is preferably from 2 to 10 mm for use in a fixed bed system and from powder to 5 mm for use in a fluid bed system, though it varies depending on the reaction form.

The acid catalyst for use in the present invention can be produced by any desired method. For example, a process for preparing a heteropolyacid and/or heteropolyacid salt catalyst is described below, which comprises first and second steps.

First Step:

A step for obtaining a solution or suspension of a heteropolyacid and/or a heteropolyacid salt.

Second Step:

A step for supporting the solution or suspension obtained in the first step on a support.

The solvent which can be used in the first step is

not particularly limited as long as it can uniformly dissolve or suspend the desired heteropolyacid and/or heteropolyacid salt, and water, an organic solvent or a mixture thereof may be used. Preferred examples thereof include water, alcohols and carboxylic acids, but the present invention is not limited thereto.

The method for dissolving or suspending a heteropolyacid and/or a heteropolyacid salt in the solvent is not particularly limited and any method may be used as long as it can uniformly dissolve or suspend a desired heteropolyacid and/or heteropolyacid salt.

For example, in the case of a heteropolyacid, namely, a free acid, if it can dissolve, the heteropolyacid may be dissolved as it is. Even when the heteropolyacid cannot completely dissolve, if the heteropolyacid can be uniformly suspended by forming it into fine powder, the heteropolyacid may be suspended as such. In the case of a heteropolyacid salt, a method of dissolving a heteropolyacid and a starting material salt for a neutralizing element together or separately and then mixing them to prepare a uniform solution or suspension may be used. Furthermore, in the case of a compound which is in the state of a heteropolyacid salt, a uniform solution or suspension may be obtained in the same manner as in the heteropolyacid.

The optimal volume of the solution or suspension varies depending on the supporting method in the second step and the support used but this is not particularly limited.

The second step is a step for supporting a solution or suspension of a heteropolyacid and/or a heteropolyacid salt obtained in the first step on a support to obtain a catalyst for use in the manufacture of a lower aliphatic ester.

The method for bearing the solution or suspension of a heteropolyacid and/or a heteropolyacid salt on a support is not particularly limited and a known method

may be used.

For example, the catalyst may be prepared by dissolving or suspending a heteropolyacid and/or a heteropolyacid salt in a solvent so as to form a solution or suspension corresponding to the liquid absorption amount of the support and impregnating a support with the solution or suspension.

The catalyst may also be prepared by using an excess solution or suspension, impregnating it into a support while moderately moving the support in the solution or suspension of a heteropolyacid and/or a heteropolyacid salt and then removing the excess acid through filtration.

The wet catalyst obtained as such is preferably dried by placing it in a heating oven for a few hours. Thereafter, the catalyst is cooled to the ambient temperature in a desiccator. The drying temperature is not particularly limited but if it exceeds about 400°C, the skeleton of the heteropolyacid may be disadvantageously destroyed. The drying temperature is preferably from 80 to 350°C.

Industrially, the catalyst may be continuously dried using a dryer such as through-flow rotary dryer, continuous fluidized bed dryer or continuous hot air carrier type dryer.

The amount of the heteropolyacid and/or heteropolyacid salt supported can be calculated simply by subtracting the mass of the support used from the dry mass of the catalyst prepared. A more exact amount may be measured by chemical analysis such as ICP (inductively coupled plasma emission spectrometry).

In practicing the process for producing an ester of the present invention, the ratio between ethylene and the carboxylic acid used is preferably such that ethylene is used in an equimolar amount or excess molar amount to the carboxylic acid. The ratio of ethylene : carboxylic acid is preferably, as a molar ratio, from 1:1 to 30:1, more

preferably from 3:1 to 20:1, still more preferably from 5:1 to 15:1.

5 In the process of the present invention, the vapor phase reaction may be performed in either a fixed bed system or a fluidized bed system. The shape of the support may also be selected from those formed into a size of from powder to a few mm in diameter according to the system of the practice.

10 In the process of the present invention, a slight amount of water is preferably mixed in the starting materials from the standpoint of the catalyst life. However, if an excessively large amount of water is added, by-products such as alcohol and ether may disadvantageously increase. In general, the amount of
15 water is preferably from 1 to 15 mol%, more preferably from 2 to 8 mol%, in the entire amount of the olefin and carboxylic acid used.

20 The reaction temperature and pressure must be in the range capable of keeping the supply medium in a gaseous form and varies depending on the starting materials used. In general, the reaction temperature is preferably from 120 to 250°C, more preferably from 140 to 220°C.

25 The pressure is preferably from atmospheric pressure to 3 MPa, more preferably from atmospheric pressure to 2 MPa.

With respect to the space velocity (GHSV) of the raw materials, these preferably pass through the catalyst layer at a GHSV of from 100 to 7,000/hr, more preferably from 300 to 3,000/hr.

30 The present invention is further illustrated below by referring to the examples and reference examples. However, these examples are only for describing the embodiments of the present invention, and the present invention should not be construed as being limited
35 thereto.

Analysis of Reaction Gas

In Examples 1 to 12 and Comparative Examples 1 to 7

which are examples of the one-path process having no recycle system, the starting material composition fed to the reactor was used as the inlet gas concentration.

In Examples 13 to 15 and Comparative Example 8 which are examples of the process having a recycle system, for a gas at the inlet of the reactor, when a predetermined time was passed after the initiation of the reaction, a part of the gas was sampled by a three-way valve and cooled and the concentrated solution collected was recovered in the whole amount and analyzed by gas chromatography. With respect to the effluent gas remaining uncondensed, the flow rate of the gas at the outlet discharged within the sampling time was measured and a part of the gas was sampled and analyzed on the composition by gas chromatography. On the other hand, for a gas at the outlet, the whole amount of the gas was cooled and the concentrated reaction solution collected was recovered in the whole amount and analyzed by gas chromatography. With respect to the effluent gas remaining uncondensed, the flow rate of the gas at the outlet discharged within the sampling time was measured and a part of the gas was sampled and analyzed on the composition by gas chromatography. The analysis conditions are shown below.

Conditions for Analysis of Uncondensed Gas

An absolute calibration curve method was used for the analysis. The analysis was performed under the following conditions by sampling 50 ml of the effluent gas and allowing the whole amount thereof to flow into a 1 ml-volume gas sampler attached to the gas chromatograph.

1. Ether, Carboxylic Acid Ester, Alcohol, Trace By-Products

Gas chromatography:

gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler (MGS-4, measuring tube: 1 ml) for Shimadzu gas chromatograph

Column:

packed column SPAN80 15% Shinchrom A, 60 to 80 mesh
(length: 5 m)

Carrier gas:

5 nitrogen (flow rate: 25 ml/min)

Temperature conditions:

constant temperature conditions where the detector
and the vaporization chamber were at 120°C and the
column was at 65°C

10 Detector:

FID (H₂ pressure: 60 kPa, air pressure: 100 kPa)

2. Butene

Gas chromatography:

15 gas chromatograph (GC-14B, manufactured by Shimadzu
Corporation) with a gas sampler (MGS-4, measuring
tube: 1 ml) for Shimadzu gas chromatograph

Column:

packed column Unicarbon A-400, length: 2 m

Carrier gas:

20 helium (flow rate: 23 ml/min)

Temperature conditions:

the temperatures of the detector and the
vaporization chamber were 120°C and the column
temperature was elevated from 40°C to 95°C at a
25 temperature increasing rate of 40°C/min

Detector:

FID (H₂ pressure: 70 kPa, air pressure: 100 kPa)

3. Ethylene

Gas chromatography:

30 gas chromatograph (GC-14B, manufactured by Shimadzu
Corporation) with a gas sampler (MGS-4, measuring
tube: 1 ml) for Shimadzu gas chromatograph

Column:

packed column Unibeads 1S, length: 3 m

35 Carrier gas:

helium (flow rate: 20 ml/min)

Temperature conditions:

constant temperature conditions where the detector and the vaporization chamber were at 120°C and the column was at 65°C

5 Detector:

TCD (He pressure: 70 kPa, current: 90 mA, temperature: 120°C)

Analysis of Collected Solution

10 The analysis was performed using the internal standard method, where the analysis solution was prepared by adding 1 ml of 1,4-dioxane as the internal standard to 10 ml of the reaction solution and 0.4 µl of the analysis solution was injected.

Gas chromatography:

15 GC-14B, manufactured by Shimadzu Corporation

Column:

capillary column TC-WAX (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 µm)

Carrier gas:

20 nitrogen (split ratio: 20, column flow rate: 2 ml/min)

Temperature conditions:

25 the temperatures of the detector and the vaporization chamber were both 200°C and the column was kept at 50°C for 5 minutes from the initiation of the analysis, thereafter rising to 150°C at a temperature increasing rate of 20°C/min, and kept at 150°C for 10 minutes

Detector:

30 FID (H₂ pressure: 70 kPa, air pressure: 100 kPa)
Support

Support 1:

35 natural silica (KA-0, produced by SUD-CHEMIE AG)
(specific surface area: 68.5 m²/g, pore volume: 0.71 cm³/g)

Support 2:

synthetic silica (CARiACT Q-10, produced by Fuji
Silicia Kagaku K.K.) (specific surface area: 219.8
m²/g, pore volume: 0.660 cm³/g)

5 Support 3:

natural silica (KA-1, produced by SUD-CHEMIE AG)
(specific surface area: 113 m²/g, pore volume: 0.64
cm³/g)

Support 4:

10 natural silica (KA-160, produced by SUD-CHEMIE AG)
(specific surface area: 130 m²/g, pore volume: 0.53
cm³/g)

Support 5:

15 synthetic silica (CARiACT Q-6, produced by Fuji
Silicia Kagaku K.K.) (specific surface area: 450
m²/g, pore volume: 0.6 cm³/g)

Support 6:

20 synthetic silica (CARiACT Q-15, produced by Fuji
Silicia Kagaku K.K.) (specific surface area: 200
m²/g, pore volume: 1.0 cm³/g)

Support 7:

synthetic silica (CARiACT Q-30, produced by Fuji
Silicia Kagaku K.K.) (specific surface area: 100
m²/g, pore volume: 1.0 cm³/g)

25 Support 8:

synthetic silica (N-602A, produced by Nikki Kagaku
K.K.) (specific surface area: 290 m²/g, pore volume:
0.8 cm³/g)

Support 9:

30 synthetic silica (N-601A3, produced by Nikki Kagaku
K.K.) (specific surface area: 264 m²/g, pore volume:
0.9 cm³/g)

Support 10:

35 synthetic silica (N-602T, produced by Nikki Kagaku
K.K.) (specific surface area: 132 m²/g, pore volume:
0.7 cm³/g)

Preparation Process of Catalyst 1

The support 1 was dried for 4 hours in a (hot air) dryer previously adjusted to 110°C. 1 L of the previously dried carrier was subjected to the measurement of the bulk density by a 1 L-volume messcylinder. Tungstophosphoric acid and lithium nitrated were added each to the weight shown in Table 1, 15 ml of pure water was added thereto, and the mixture was uniformly dissolved to obtain a $\text{Li}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$ aqueous solution (impregnating solution). This impregnating solution was charged into the messcylinder and pure water was added to reach the liquid amount shown in the amount of prepared solution in Table 1 and then uniformly stirred. The previously dried support was weighed to the amount described in Table 1, added to the impregnating solution and thoroughly stirred, thereby impregnating the support. The support impregnated with the solution was air dried for 1 hour and thereafter dried for 5 hours by a hot air dryer adjusted to 150°C. The weight of the catalyst obtained was measured.

Preparation Process of Catalysts 2 to 12

The preparation was performed as described in Preparation Process of Catalyst 1 by changing the kind and weight of the support, the kind and weight of the catalyst component and the weight of lithium nitrate as shown in Table 1. The catalyst was supported on the support in the same manner as in Preparation Process of Catalyst 1.

Table 1

Name of Catalyst	Support	Bulk Density (g/L)	Weight of Support (g)	Kind of Catalyst Component	Amount of Catalyst Component (g)	Amount of Lithium Nitrate (g)	Volume of Prepared Solution (ml)	Dry Weight (g)
catalyst 1	1	558	55.8	HPW	65.33	0.1318	34	113.6
catalyst 2	2	456	45.6	HSiW	34.88	0.0719	43	75.6
catalyst 3	3	573	57.3	HPW	65.33	0.1318	33	124.5
catalyst 4	4	575	57.5	HPW	65.33	0.1318	32	113.8
catalyst 5	5	627	62.7	HSiW	34.88	0.0719	33	94.3
catalyst 6	6	446	44.6	HSiW	34.88	0.0719	40	75.2
catalyst 7	7	432	43.2	HSiW	34.88	0.0719	41	74.5
catalyst 8	8	811	81.1	HPW	35.63	0.0718	64	114.7
catalyst 9	9	703	70.3	HPW	35.63	0.0718	83	102.9
catalyst 10	10	813	81.3	HPW	35.63	0.0718	69	114.3
catalyst 11	2	456	45.6	HPVW	35.90	0.0753	43	76.3
catalyst 12	2	456	45.6	HSiVW	35.90	0.0753	43	75.9

HPW: $H_3PW_{12}O_{40}$
 HSiW: $H_4SiW_{12}O_{40}$
 HPVW: $H_4PVW_{12}O_{40}$
 HSiVW: $H_5SiVW_{12}O_{40}$

Example 1

40 ml of the catalyst obtained by Preparation
Process of Catalyst 1 was filled in a reaction tube and a
mixed gas of ethylene : acetic acid : steam : nitrogen
5 shown in Table 2 was introduced thereinto at a
temperature of 165°C and a pressure of 0.8 MPaG (gauge
pressure) to perform the reaction. The results are shown
in Table 3.

Table 2

	Catalyst	Starting Material Gas, ethylene:acetic acid: water:nitrogen: substance added (molar ratio)	Substance Added (ppm) *1	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Reaction Time (hr)	Reaction Temperature (°C)
Example 1	1	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 2	2	78.5:8.0:4.5:9.0	none	60.0	0.8	5 99 5 100	165
Example 3	3	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 4	4	78.5:8.0:4.5:9.0	none	60.0	0.8	5 103	165
Example 5	5	78.5:8.0:4.5:9.0	none	60.0	0.8	5 98	165
Example 6	6	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 7	7	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 8	8	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 9	9	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 10	10	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 11	11	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 12	12	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Comparative Example 1	1	78.5:8.0:4.5:8.2:0.8	1-butene (10088)	60.5	0.8	5 100	165

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TMP:	2,2,4-trimethylolpentane
2-BEE:	2-butyl ethyl ether
2-BA:	2-butyl acetate
2-BuOH:	2-butyl alcohol
*1:	concentration (ppm) when additive/(ethylene + substance added)

2,2,4-trimethylolpentane
2-butyl ethyl ether
2-butyl acetate
2-butyl alcohol
concentration (ppm) when
*1:

Table 3

	Catalyst	Substance Added (ppm) *1	STY of Ethyl Acetate (g/L- hr)	Trace By- Products (wt%)
Example 1	1	none	191	0.0047
			186	0.0123
Example 2	2	none	252	0.0001
			236	0.0007
Example 3	3	none	212	0.0004
			204	0.0160
Example 4	4	none	224	0.0127
			213	0.0234
Example 5	5	none	268	0.0003
			251	0.0010
Example 6	6	none	189	0.0003
			180	0.0005
Example 7	7	none	130	0.0004
			125	0.0008
Example 8	8	none	178	0.0009
			169	0.0012
Example 9	9	none	95	0.0006
			90	0.0010
Example 10	10	none	205	0.0303
			185	0.0011
Example 11	11	none	148	0.0303
			140	0.0400
Example 12	12	none	139	0.0160
			131	0.0250

*1: concentration (ppm) when additive/(ethylene + substance added)

5 Examples 2 to 12

The reactions were performed in the same manner as in Example 1 except for changing Catalyst 1 in Example 1 to Catalysts 2 to 12 as shown in Table 2. The results are shown in Table 3.

10 Comparative Examples 1, 2, 3, 5 and 6

The reactions were performed in the same manner as

in Example 1 except for changing the reaction gas composition as shown in Table 2. The results are shown in Table 4. As compared with Example 1, the STY of ethyl acetate after about 100 hours seriously decreased, trace by-products increased and a part was separated from the reaction solution and became oily.

Table 4

	Catalyst	Substance Added (ppm) *1	STY of Ethyl Acetate (g/L-hr)	Trace By-Products (wt%)
Comparative Example 1	1	1-butene (10088)	200	2.4277
			166	5.3126
Comparative Example 2	1	2-octene (10088)	66	Oil was produced.
			43	Oil was produced.
Comparative Example 3	1	TMP (10088)	197	Oil was produced.
			171	Oil was produced.
Comparative Example 4	2	1-butene (19975)	203	6.3111
			165	8.2766
Comparative Example 5	1	2-BA (19975)	192	1.9833
			153	3.5211
Comparative Example 6	1	2-BuOH (19975)	195	1.5633
			177	3.0122
Comparative Example 7	2	2-BEE (15056)	203	6.3111
			181	7.2812

TMP: 2,2,4-trimethylolpentane

2-BEE: 2-butyl ethyl ether

2-BA: 2-butyl acetate

2-BuOH: 2-butyl alcohol

*1: concentration (ppm) when additive/(ethylene + substance added)

Comparative Examples 4 and 7

The reactions were performed in the same manner as in Example 2 except for changing the reaction gas composition as shown in Table 2. The results are shown in Table 4. As compared with Example 2, the STY of ethyl acetate seriously decreased and trace by-products increased.

Example 13

750 ml of the catalyst shown in Table 5 was filled in a reactor of a reaction apparatus schematically shown in Fig. 3. The conditions were set such that the temperature of the reactor was 160°C, the temperature of the vaporizer was 180°C, the pressure of the entire system was 0.8 MPaG (gauge pressure) and the condensation temperature in the scrubber was -5°C. The amount of ethylene fed in Fig. 3 was 49.0 g/hr and the gas not condensed in the scrubber was recycled by a compressor. Other conditions are shown in Table 5.

Table 5

	Catalyst	Gas Composition in (1) after the reaction for 100 Hours, ethylene:acetic acid:water:nitrogen:ethyl acetate:butene (molar ratio)	Butene Concen- tration (ppm)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temper- ature of Scrubber (°C)	Reaction Time (hr)	Reaction Temper- ature (°C)	STY of Ethyl Acetate (g/L-hr)	Trace By- Products (wt%)
Example 13	1	78.5:8.0:4.5:8.8:0.2:0.0016	20	1125	0.8	-5	100	165	181	0.0056
							500		183	0.0053
Example 14	2	78.5:8.0:4.5:8.7:0.2:0.0950	1200	1125	0.8	10	100	165	240	0.0005
							500		228	0.0010
Example 15	1	78.5:8.0:4.5:8.5:0.2:0.318	4000	1125	0.8	30	100	165	175	0.0086
							500		148	0.0090
Comparative Example 8	1	78.5:8.0:4.5:7.8:0.2:0.953	12000	1125	0.8	60	100	165	160	5.9030
							500		73	6.3310

After starting the feeding of raw materials, the inlet concentration (analysis value at (1) of Fig. 3) was stabilized within 50 hours, therefore, the operation was continued as it is. The reaction results calculated from the inlet concentration and the reaction gas concentration at the outlet (analysis value at (3) of Fig. 3) after 100 hours or 500 hours are shown in Table 5.

Examples 14 and 15 and Comparative Example 8

The reactions were performed in the same manner as in Example 13 except for changing the catalyst, the butene concentration and the temperature in the scrubber to the conditions shown in Table 5.

The reaction results are shown in Table 5.

Industrial Applicability

As described above, in the process for producing an ester from a carboxylic acid and an ethylene in the presence of an acid catalyst, when the concentration of olefin having 3 or more carbon atoms in the raw materials is controlled to 10,000 ppm or less in terms of a molar ratio to the total of the olefin and ethylene or when the concentration of olefin equivalent in the raw materials is controlled to 50,000 ppm or less in terms of a molar ratio to the total of the olefin equivalent and ethylene, a stable operation can be continuously performed for a long period of time.

CLAIMS

1. A process for producing an ester, comprising reacting a carboxylic acid and ethylene in the presence of an acid catalyst in a vapor phase, wherein the
5 concentration of olefin having 3 or more carbon atoms in the starting materials is 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene.

2. The process as claimed in claim 1, wherein the concentration of olefin having 3 or more carbon atoms in
10 the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene.

3. The process as claimed in claim 2, wherein the concentration of olefin having 3 or more carbon atoms in
15 the starting materials is 1,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene.

4. The process as claimed in any one of claims 1 to 3, wherein the olefin having 3 or more carbon atoms comprises at least one compound selected from the group consisting of trans-2-butene, cis-2-butene and 1-butene.

20 5. A process for producing an ester, comprising reacting a carboxylic acid and ethylene in the presence of an acid catalyst in a vapor phase, wherein the concentration of olefin equivalent in the starting materials is 50,000 ppm or less in terms of the molar
25 ratio to the total of the olefin equivalent and ethylene.

6. The process as claimed in claim 5, wherein the concentration of olefin equivalent in the starting materials is 25,000 ppm or less in terms of the molar ratio to the total of the olefin equivalent and ethylene.

30 7. The process as claimed in claim 6, wherein the concentration of olefin equivalent in the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of the olefin equivalent and the ethylene.

35 8. The process as claimed in any one of claims 5 to 7, wherein the olefin equivalent comprises at least one compound selected from the group consisting of

saturated alcohols having 3 or more carbon atoms, esters of a carboxylic acid and a saturated alcohol having 3 or more carbon atoms, and saturated ethers having 5 or more carbon atoms.

5 9. A process for producing an ester, comprising reacting a carboxylic acid and ethylene in the presence of an acid catalyst in a vapor phase, wherein the sum of the concentration of olefin having 3 or more carbon atoms and one-fifth the concentration of olefin equivalent in
10 the starting materials is 10,000 ppm or less in terms of the molar ratio to the total of the olefin and olefin equivalent and ethylene.

15 10. The process as claimed in claim 9, wherein the sum of the concentration of olefin having 3 or more carbon atoms and one-fifth the concentration of olefin equivalent in the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of the olefin and olefin equivalent and ethylene.

20 11. The process as claimed claim 10, wherein the sum of the concentration of olefin having 3 or more carbon atoms and one-fifth the concentration of olefin equivalent in the starting materials is 1,000 ppm or less in terms of the molar ratio to the total of the olefin and olefin equivalent and ethylene.

25 12. The process as claimed in any one of claims 9 to 11, wherein the olefin having 3 or more carbon atoms comprises at least one compound selected from the group consisting of trans-2-butene, cis-2-butene and 1-butene.

30 13. The process as claimed in any one of claims 9 to 12, wherein the olefin equivalent comprises at least one compound selected from the group consisting of saturated alcohols having 3 or more carbon atoms, esters of a carboxylic acid and a saturated alcohol having 3 or more carbon atoms, and saturated ethers having 5 or more
35 carbon atoms.

 14. The process as claimed in any one of claims 1 to 13, wherein the carboxylic acid and ethylene is

reacted in the presence of water.

15. The process as claimed in any one of claims 1 to 14, wherein the carboxylic acid is at least one of lower aliphatic carboxylic acids having from 1 to 4 carbon atoms.

16. The process as claimed in any one of claims 1 to 15, wherein the acid catalyst comprises at least one compound selected from heteropolyacids and heteropolyacid salts.

17. The process as claimed in claim 16, wherein the heteropolyacid comprises at least one compound selected from the group consisting of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid, phosphovanadomolybdic acid, molybdotungstosilicic acid and molybdotungstophosphoric acid.

18. The process as claimed in claim 16, wherein the heteropolyacid salt comprises at least one compound selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, barium, copper, gold, gallium and ammonium salts of heteropolyacids.

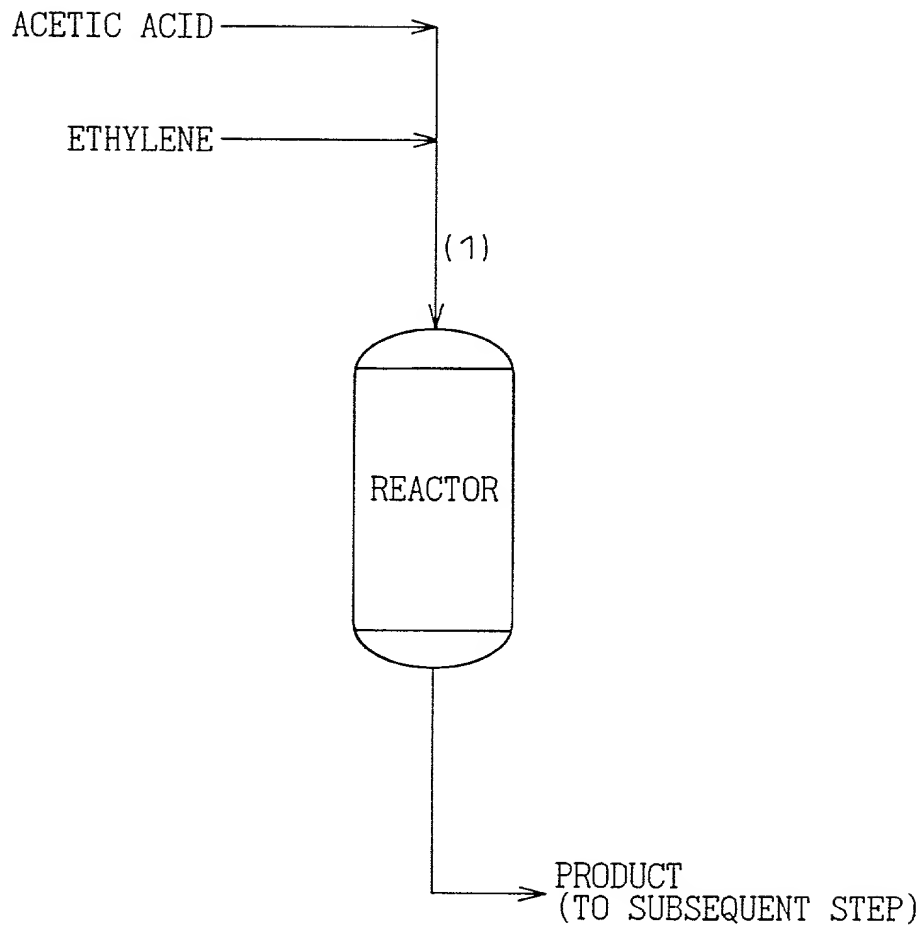
ABSTRACT

A process for producing an ester comprising reacting a carboxylic acid and ethylene in the presence of an acid catalyst in a vapor phase, wherein the concentration of olefin having 3 or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene. The deterioration of the catalyst can be remarkably prevented from proceeding and a continuous and stable operation can be performed for a long time.

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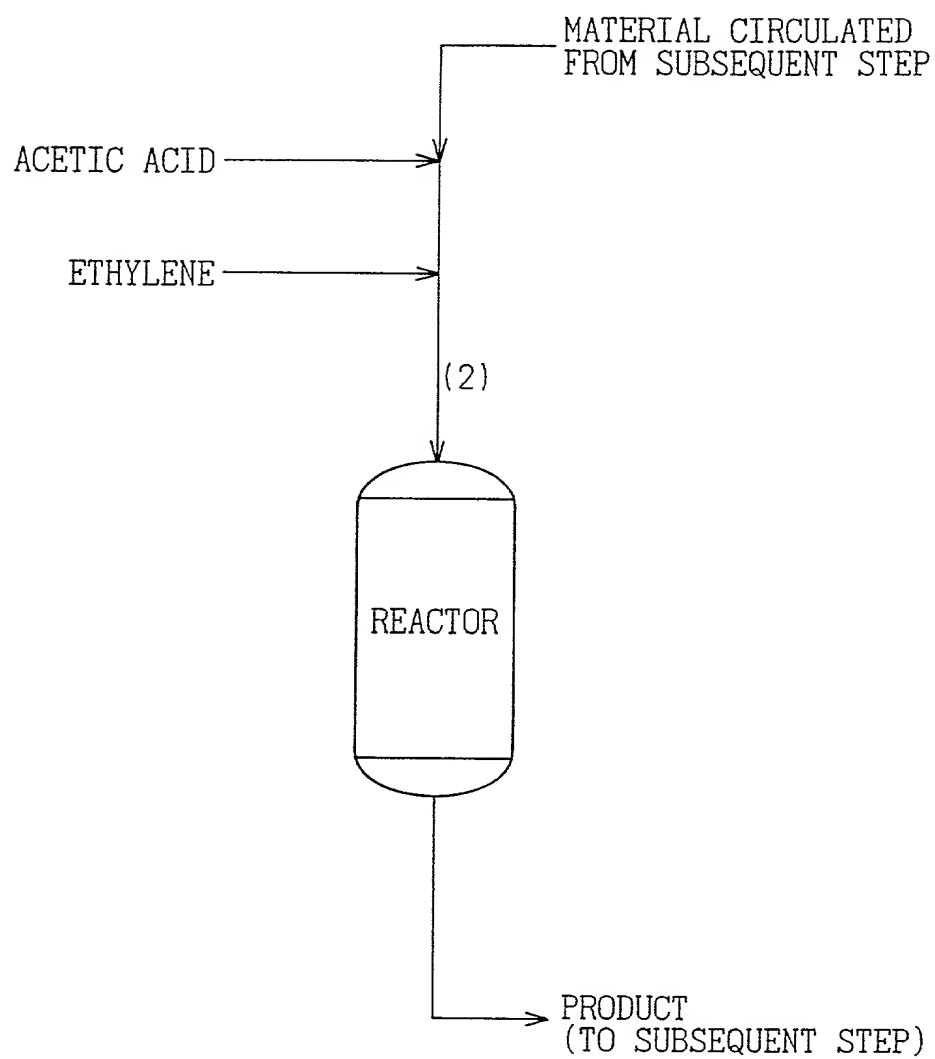
Fig. 1



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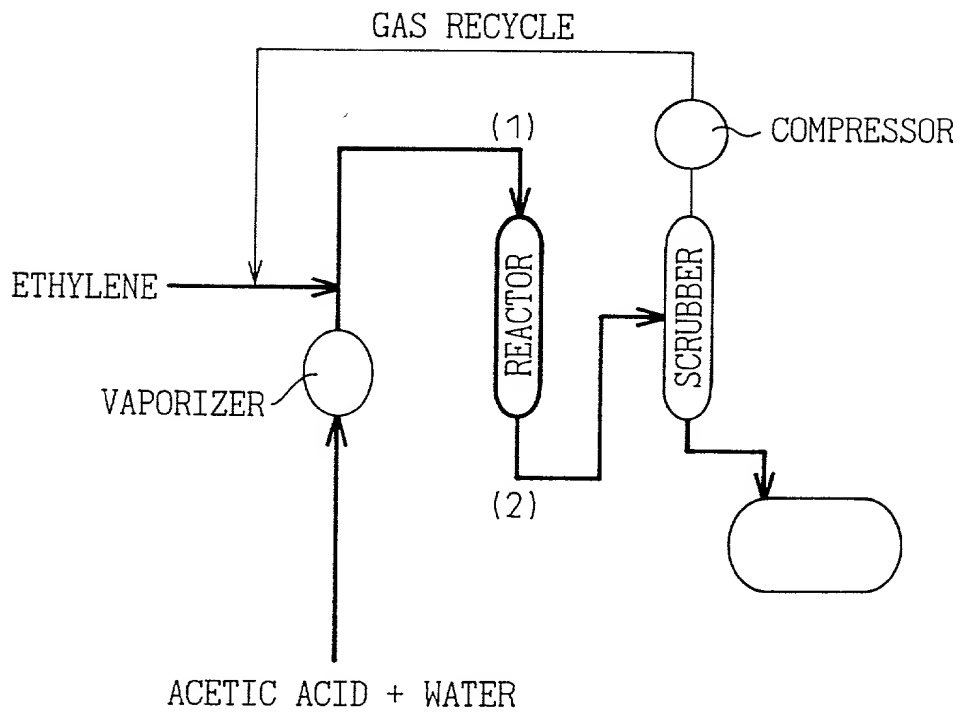
Fig.2



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Fig.3



Japanese Language Declaration

日本語宣言書

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(Supply similar information and signature for third and
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Prior foreign application(s)
外国での先行出願

[C1] 11-301780 (Pat. Appln.) [C2] Japan
(Number) (Country)
(番号) (国名)
2000-49627

[C5] (Pat. Appln.) [C6] Japan
(Number) (Country)
(番号) (国名)

[C9] [C10]
(Number) (Country)
(番号) (国名)

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(Application No.) (Filing Date)
(出願番号) (出願日)

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[E1] No. [E2]
(Application No.) (Filing Date)
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Priority Not Claimed
優先権主張なし

[C3] 25/October/1999 ☐
(Day/Month/Year Filed)
(出願年月日)

[C7] 25/February/2000 ☐
(Day/Month/Year Filed)
(出願年月日)

[C11] ☐
(Day/Month/Year Filed)
(出願年月日)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

[D3] 60/192,880 (Pat. [D4] 29/March/2000
(Application No.) Appln.) (Filing Date)
(出願番号) (出願日)

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[E3]
(Status)(patented, pending, abandoned)
(現況: 特許許可済、係属中、放棄済)

[E6]
(Status)(patented, pending, abandoned)
(現況: 特許許可済、係属中、放棄済)

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私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR PRODUCING ESTERS

上記発明の明細書（下記の欄でx印がついていない場合は、本書に添付）は、

the specification of which is attached hereto unless the following box is checked:

☐ 月 日に提出され、米国出願番号または特許協定条約国際出願番号を _____ とし、
（該当する場合） _____ に訂正されました。

☐ was filed on October 24, 2000
as United States Application Number or PCT
International Application Number PCT/JP00/07443
and was amended on
[B2] (if applicable)

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

Japanese Language Declaration

日本語宣言書

第三の共同発明者の氏名 (該当する場合)		Full name of third joint inventor, if any
同第三発明者の署名	日付	Etsuko Kadowaki
住所		Third inventor's signature Etsuko Kadowaki
国籍		Date December 1, 2000
郵便の宛先		Residence Oita-shi, Oita, Japan
		Citizenship Japanese
		Post office address c/o OITA PLANT, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 Japan
第四の共同発明者の氏名 (該当する場合)		Full name of fourth joint inventor, if any
同第四発明者の署名	日付	Takashiye Miyanari
住所		Fourth inventor's signature Takashiye Miyanari
国籍		Date December 1, 2000
郵便の宛先		Residence Oita-shi, Oita, Japan
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第五の共同発明者の氏名 (該当する場合)		Full name of fifth joint inventor, if any
同第五発明者の署名	日付	Wataru Oguchi
住所		Fifth inventor's signature Wataru Oguchi
国籍		Date December 1, 2000
郵便の宛先		Residence Oita-shi, Oita, Japan
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第六の共同発明者の氏名 (該当する場合)		Full name of sixth joint inventor, if any
同第六発明者の署名	日付	
住所		Sixth inventor's signature
国籍		Date
郵便の宛先		Residence
		Citizenship
		Post office address